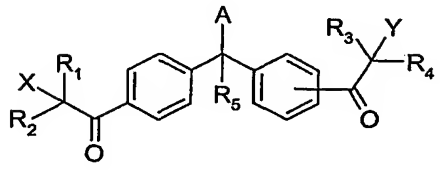
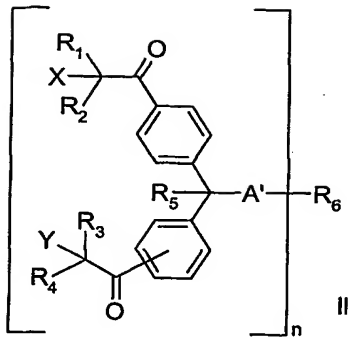
Claims:

1. A photoinitiator of formula I or II



I



II

wherein

R_1, R_2, R_3 and R_4 are each independently of the others C_1-C_8alkyl; C_1-C_4alkyl substituted by OH, C_1-C_4alkoxy, -CN, -COO(C_1-C_8alkyl), (C_1-C_4alkyl)-COO-, benzyl, phenyl or by -N(R_{13})(R_{14}); C_3-C_6alkenyl, benzyl, -CH_2-C_6H_4-(C_1-C_4alkyl) or phenyl; or

R_1 and R_2 together and / or R_3 and R_4 together are unbranched or branched C_2-C_9alkylene or C_3-C_6-oxa- or -aza-alkylene;

R_5 is hydrogen, C_1-C_8alkyl, C_3-C_6alkenyl, benzyl, -CH_2-C_6H_4-(C_1-C_4alkyl) or phenyl;

A is Cl, Br, -O-R_7, -NR_8R_9 or -S-R_{16};

A' is -O-, -NH- or -NR_8-;

X and Y are each independently of the other -O-R_{10} or -N(R_{11})(R_{12});

n is an integer from 1 to 10, preferably an integer from 1 to 4, especially 1, 2 or 3;

R_6 is an n-valent radical of linear or branched C_2-C_{20}alkyl the carbon chain of which may be interrupted by cyclohexanediyl, phenylene, -CH(OH)-, -C(C_2H_5)(CH_2-CH_2-OH)-, -C(CH_3)(CH_2-CH_2-OH)-, -C(CH_2-CH_2-OH)$_2$-, -N(CH_3)-, -N(C_2H_5)-, -N(CH_2-CH_2-OH)-, -CO-O-, -O-CO-, -O-CO-NH, NH-CO-O-, -P(CH_2-CH_2-OH)-, -P(O)(CH_2-CH_2-OH)-, -O-P(O-CH_2-CH_2-OH)-O-, -O-P(O)(O-CH_2-CH_2-OH)-O-, -O-cyclohexanediyl-C(CH_3)$_2$-cyclohexanediyl-O-,
-O-phenylene-C(CH_3)$_2$-phenylene-O-, -O-phenylene-CH_2-phenylene-O-, -Si(CH_3)$_2$-, -O-Si(CH_3)$_2$-O-, -O-Si(CH_3)(O-CH_3)-O-, -Si(CH_3)(R_{17})-O-Si(CH_3)(R_{18})-, 5-(2-hydroxy-ethyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl and/or by from one to nine oxygen atoms, or

R_6 is an n-valent radical of linear or branched -CO-NH-(C_2-C_{16}alkylene)-(NH-CO)$_{n-1}$- or linear or branched -CO-NH-(C_0-C_9alkylene)-(NH-CO)$_{n-1}$- which may be interrupted by

one or two phenylene, methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-isocyanatohexyl)-biuret-1,5-diyl or 5-(6-isocyanatohexyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl radical(s), or

R_6 is an n-valent radical of linear or branched -CO-(C_0-C_{12}alkylene)-$(CO)_{n-1}$- and the alkylene may be interrupted by oxygen, phenylene, cyclohexanediyl or by norbornanediyl; , or

R_6 is an n-valent radical of linear or branched –C_2-C_{50}alkylene the carbon chain of which is interrupted by one to 15 oxygen, and may be subsituted by OH or NH_2;

R_7 is hydrogen, -Si(C_1-C_6alkyl)$_3$, C_1-C_{12}alkyl, R_{21}, C_2-C_{18}acyl, -CO-NH-C_1-C_{12}alkyl, C_2-C_{20}hydroxyalkyl, C_2-C_{20}methoxyalkyl, 3-(C_1-C_{18}alkoxy)-2-hydroxy-propyl, 3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]-propyl, 2,3-dihydroxy-propyl or linear or branched C_2-C_{21}hydroxyalkyl or (C_1-C_4alkoxy)-C_2-C_{21}alkyl the carbon chain of which is interrupted by from one to nine oxygen atoms;

R_8 and R_9 are each independently of the other hydrogen, C_1-C_{12}alkyl,; C_2-C_4alkyl substituted by one or more of the groups OH, C_1-C_4alkoxy, -CN, -COO(C_1-C_4alkyl); C_3-C_5alkenyl, cyclohexyl or C_7-C_9phenylalkyl, or

when R_9 = H or methyl, R_8 is also C_2-C_{50}alkyl substituted by one or more of the groups methyl, ethyl, OH, NH_2, and is interrupted by one or more oxygen, -NH-, cyclohexanediyl, norbornanediyl or phenylene, or

R_8 and R_9 together are unbranched or branched C_3-C_9alkylene which may be interrupted by -O- or by -N($\mathbf{R}_{15}$)-;

R_{10} is hydrogen, -Si(C_1-C_6alkyl)$_3$, C_1-C_8alkyl, C_3-C_6alkenyl or benzyl,

R_{11} and R_{12} are each independently of the other C_1-C_{12}alkyl; C_2-C_4alkyl substituted by one or more of the groups OH, C_1-C_4alkoxy, -CN, -COO(C_1-C_4alkyl); C_3-C_5alkenyl, cyclohexyl or C_7-C_9phenylalkyl, or

R_{11} and R_{12} together are unbranched or branched C_3-C_9alkylene which may be interrupted by -O- or by -N($\mathbf{R}_{15}$)-;

R_{13} and R_{14} are each independently of the other hydrogen, C_1-C_{12}alkyl; C_2-C_4alkyl substituted by one or more of the groups OH, C_1-C_4alkoxy, -CN, -COO(C_1-C_4alkyl); C_3-C_5alkenyl, cyclohexyl or C_7-C_9phenylalkyl, or

R_{13} and R_{14} together are unbranched or branched C_3-C_9alkylene which may be interrupted by -O- or by -N($\mathbf{R}_{15}$)-;

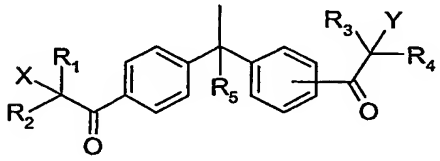
R_{15} is hydrogen, C_1-C_4alkyl, allyl, benzyl, C_1-C_4hydroxyalkyl, $-CH_2CH_2-COO(C_1-C_4alkyl)$ or $-CH_2CH_2CN$;

R_{16} is C_1-C_{18}alkyl, hydroxyethyl, 2,3-dihydroxypropyl, cyclohexyl, benzyl, phenyl, C_1-C_{12}alkylphenyl, $-CH_2-COO(C_1-C_{18}alkyl)$, $-CH_2CH_2-COO(C_1-C_{18}alkyl)$ or $-CH(CH_3)-COO(C_1-C_{18}alkyl)$;

R_{17} and R_{18} are each independently of the other a monovalent radical methyl, $-O-Si(CH_3)_3$, $-O-Si(CH_3)_2-O-Si(CH_3)_3$, $-O-Si(CH_3)[-(CH_2)_p-OH]-O-Si(CH_3)$ or a bivalent radical $-O-Si(CH_3)_2-$, $-O-Si(CH_3)[-(CH_2)_p-OH]-$, $-O-Si(CH_3)(\mathbf{R_{19}})-$, $-O-Si(CH_3)(\mathbf{R_{20}})-$ and form chains;

R_{19} and R_{20} are each independently of the other a monovalent radical methyl, $-O-Si(CH_3)_3$, $-O-Si(CH_3)_2-O-Si(CH_3)_3$, $-O-Si(CH_3)[-(CH_2)_p-OH]-O-Si(CH_3)$ or a bivalent radical $-O-Si(CH_3)_2-$, $-O-Si(CH_3)[-(CH_2)_p-OH]-$, $-O-Si(CH_3)(\mathbf{R_{19}})-$, $-O-Si(CH_3)(\mathbf{R_{20}})-$ and extend chains and, when R_{19} and R_{20} are linked into a ring, $-(R_{19})-(R_{20})-$ is the bridge -O- ;

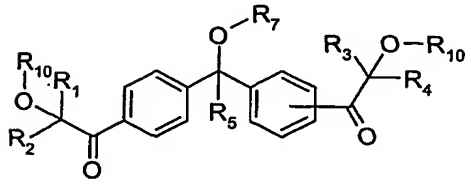
R_{21} is, independently of formula I, a radical



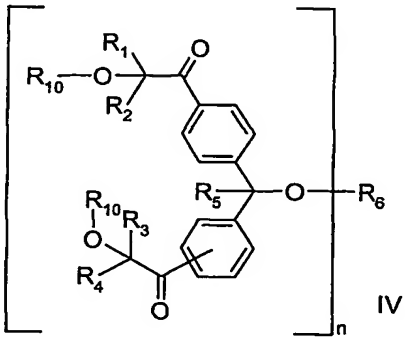
;

p is an integer from 2 to 12, preferably 3, 5 or 6, it being possible for the carbon chain of the alkylene to be interrupted by from one to three oxygen atoms.

2. A photoinitiator according to claim 1 of formula III or IV



III



IV

wherein

R_1, R_2, R_3 and R_4 are each independently of the others C_1-C_8alkyl, C_3-C_6alkenyl, benzyl, $-CH_2-C_6H_4-(C_1-C_4alkyl)$ or phenyl, or

R_1 and R_2 together and / or R_3 and R_4 together are unbranched or branched C_2-C_9alkylene;

R_5 is hydrogen, C_1-C_8alkyl, C_3-C_6alkenyl, benzyl, -CH_2-C_6H_4-(C_1-C_4alkyl) or phenyl;

n is an integer from 1 to 10, preferably an integer from 1 to 4, especially 1, 2 or 3; and

R_6 is an n-valent radical of linear or branched C_2-C_{20}alkyl the carbon chain of which may be interrupted by cyclohexanediyl, phenylene, -CH(OH)-, -$C(C_2H_5)(CH_2$-CH_2-OH)-, -$C(CH_3)(CH_2$-CH_2-OH)-, -$C(CH_2$-CH_2-$OH)_2$-, -$N(CH_3)$-, -$N(C_2H_5)$-, -$N(CH_2$-CH_2-OH)-, -CO-O-, -O-CO-, -$P(CH_2$-CH_2-OH)-, -P(O)(CH_2-CH_2-OH)-, -O-P(O-CH_2-CH_2-OH)-O-, -O-P(O)(O-CH_2-CH_2-OH)-O-, -O-cyclohexanediyl-$C(CH_3)_2$-cyclohexanediyl-O-, -O-phenylene-$C(CH_3)_2$-phenylene-O-, -O-phenylene-CH_2-phenylene-O-, -$Si(CH_3)_2$-, -O-$Si(CH_3)_2$-O-, -O-$Si(CH_3)$(O-CH_3)-O-, -$Si(CH_3)$(**R_{17}**)-O-$Si(CH_3)$(**R_{18}**)-, 5-(2-hydroxyethyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl and/or by from one to nine oxygen atoms, or

R_6 is an n-valent radical of linear or branched -CO-NH-(C_2-C_9alkylene)-$(NH\text{-}CO)_{n-1}$- or linear or branched -CO-NH-(C_0-C_9alkylene)-$(NH\text{-}CO)_{n-1}$- which may be interrupted by one or two phenylene, methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 5-(6-isocyanatohexyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl or 3-(6-isocyanatohexyl)-biuret-1,5-diyl radical(s), or

R_6 is an n-valent radical of linear or branched -CO-(C_0-C_{12}alkylene)-$(CO)_{n-1}$- and the alkylene may be interrupted by oxygen, phenylene, cyclohexanediyl or by norbornanediyl;

R_7 is hydrogen, -$Si(C_1$-C_6alkyl$)_3$, C_1-C_{12}alkyl, R_{21}, C_2-C_{18}acyl, -CO-NH-C_1-C_{12}alkyl, C_2-C_{20}hydroxyalkyl, C_2-C_{20}methoxyalkyl, 3-(C_1-C_{18}alkoxy)-2-hydroxy-propyl, 3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]-propyl, 2,3-dihydroxypropyl or linear or branched C_2-C_{21}hydroxyalkyl or (C_1-C_4alkoxy)-C_2-C_{21}alkyl the carbon chain of which is interrupted by from one to nine oxygen atoms;

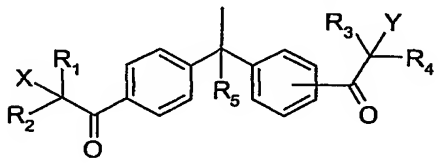
R_{10} is hydrogen, -$Si(C_1$-C_6alkyl$)(CH_3)_2$, C_1-C_8alkyl, C_3-C_6alkenyl or benzyl;

R_{17} and R_{18} are each independently of the other a monovalent radical methyl, -O-$Si(CH_3)_3$, -O-$Si(CH_3)_2$-O-$Si(CH_3)_3$, -O-$Si(CH_3)[-(CH_2)_p$-OH]-O-$Si(CH_3)$ or a bivalent radical -O-$Si(CH_3)_2$-, -O-$Si(CH_3)[-(CH_2)_p$-OH]-, -O-$Si(CH_3)$(**R_{19}**)-, -O-$Si(CH_3)$(**R_{20}**)- and form chains;

R_{19} and R_{20} are each independently of the other a monovalent radical methyl, -O-$Si(CH_3)_3$, -O-$Si(CH_3)_2$-O-$Si(CH_3)_3$, -O-$Si(CH_3)[-(CH_2)_p$-OH]-O-$Si(CH_3)$ or a bivalent radical

$-O-Si(CH_3)_2-$, $-O-Si(CH_3)[-(CH_2)_p-OH]-$, $-O-Si(CH_3)(R_{19})-$, $-O-Si(CH_3)(R_{20})-$ and extend chains and, when R_{19} and R_{20} are linked into a ring, $-(R_{19})-(R_{20})-$ is the bridge -O-;

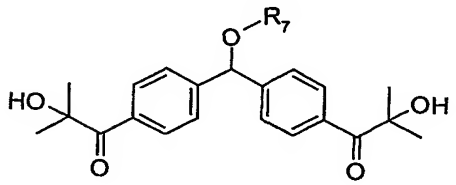
R_{21} is, independently of formula III, a radical



;

p is an integer from 2 to 12, preferably 3, 5 or 6, it being possible for the carbon chain of the alkylene to be interrupted by from one to three oxygen atoms.

3. A photoinitiator according to claim 1 of formula V

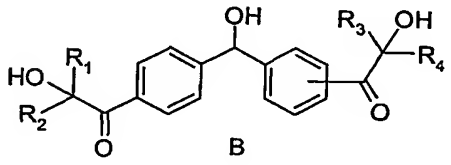


V

wherein

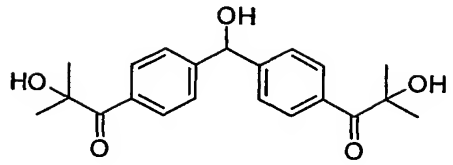
R_7 is hydrogen, $-Si(CH_3)_3$, C_1-C_8alkyl, bis[4-(2-hydroxy-2-methyl-propionyl)-phenyl]-methyl, C_2-C_{18}acyl, $-CO-NH-C_1$-C_8alkyl, C_2-C_{20}hydroxyalkyl, C_2-C_{20}methoxyalkyl or C_2-C_{20}hydroxyalkyl the carbon chain of which is interrupted by from one to nine oxygen atoms.

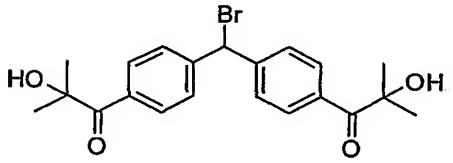
4. A photoinitiator according to claim 1 of the formula B

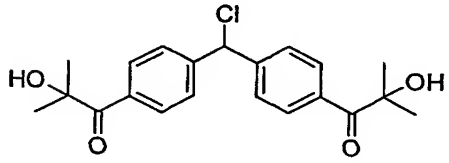


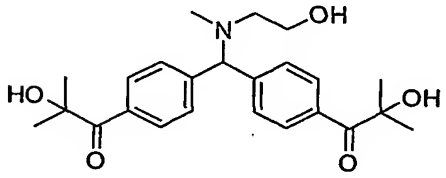
B

5. A photoinitiator according to claim 1 of formula

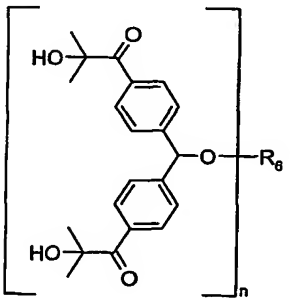




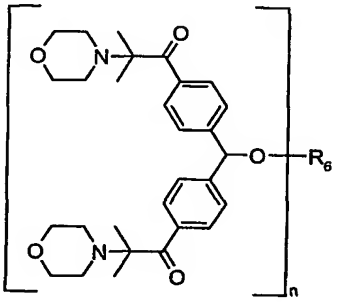




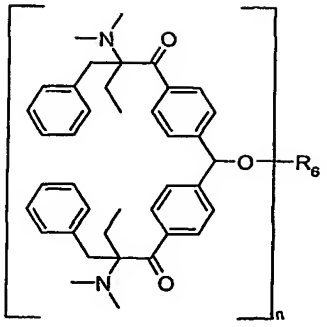
6. A photoinitiator according to claim 1 of formula VI, VII or VIII



VI



VII



VIII

wherein

n is an integer from 1 to 4, preferably an integer from 1 to 3, especially 2, and

R_6 is an n-valent radical of linear or branched C_2-C_{16}alkyl the carbon chain of which may be interrupted by cyclohexanediyl, phenylene, -CH(OH)-, -C(CH_2-CH_2-OH)$_2$-, -C(CH_3)(CH_2-CH_2-OH)-, -C(C_2H_5)(CH_2-CH_2-OH)-, -N(CH_3)-, -N(CH_2-CH_2-OH)-, -CO-O-, -O-CO-, -Si(CH_3)$_2$-, -Si(CH_3)(**R_{17}**)-O-Si(CH_3)(**R_{18}**)-, -O-Si(CH_3)$_2$-O-, -O-Si(CH_3)(O-CH_3)-O-, 5-(2-hydroxyethyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl and / or by from one to six oxygen atoms, or

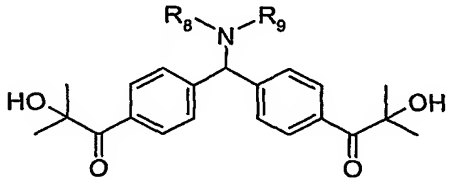
R_6 is an n-valent radical of linear or branched -CO-NH-(C_2-C_{16}alkylene)-(NH-CO)$_{n-1}$- or linear or branched -CO-NH-(C_0-C_9alkylene)-(NH-CO)$_{n-1}$- which may be interrupted by one or two phenylene, methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 5-(6-isocyanatohexyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl or 3-(6-isocyanatohexyl)-biuret-1,5-diyl radical(s),

R_{17} and R_{18} are each independently of the other a monovalent radical methyl, -O-Si(CH_3)$_3$, -O-Si(CH_3)$_2$-O-Si(CH_3)$_3$, -O-Si(CH_3)[-(CH_2)$_p$-OH]-O-Si(CH_3) or a bivalent radical -O-Si(CH_3)$_2$-, -O-Si(CH_3)[-(CH_2)$_p$-OH]-, -O-Si(CH_3)(**R_{19}**)-, -O-Si(CH_3)(**R_{20}**)- and form chains,

R_{19} and R_{20} are each independently of the other a monovalent radical methyl, -O-Si(CH_3)$_3$, -O-Si(CH_3)$_2$-O-Si(CH_3)$_3$, -O-Si(CH_3)[-(CH_2)$_p$-OH]-O-Si(CH_3) or a bivalent radical -O-Si(CH_3)$_2$-, -O-Si(CH_3)[-(CH_2)$_p$-OH]-, -O-Si(CH_3)(**R_{19}**)-, -O-Si(CH_3)(**R_{20}**)- and extend chains and, when R_{19} and R_{20} are linked into a ring, -(R_{19})-(R_{20})- is the bridge -O-,

p is an integer from 2 to 12, preferably 3, 5 or 6, it being possible for the carbon chain of the alkylene to be interrupted by from one to three oxygen atoms.

7. A photoinitiator according to claim 1 of formula IX



IX

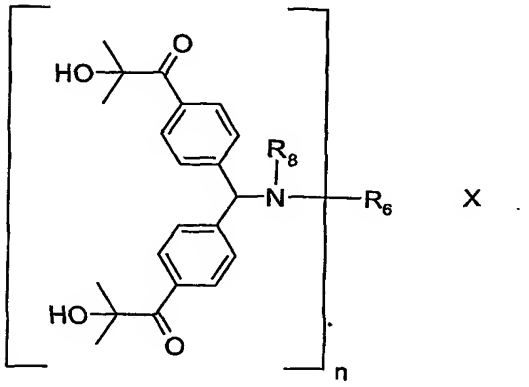
wherein

R_8 and R_9 are each independently of the other hydrogen, C_1-C_{12}alkyl,; C_2-C_4alkyl substituted by one or more of the groups OH, C_1-C_4alkoxy, -CN, -COO(C_1-C_4alkyl); C_3-C_5alkenyl, cyclohexyl or C_7-C_9phenylalkyl, or

when R_9 = H or methyl, R_8 is also C_2-C_{50}alkyl substituted by one or more of the groups methyl, ethyl, OH, NH_2, and is interrupted by one or more oxygen, -NH-, cyclohexanediyl, norbornanediyl or phenylene, or

R_8 and R_9 together are unbranched or branched C_3-C_9alkylene which may be interrupted by -O- or by -N(R_{15})-;

8. A photoinitiator according to claim 1 of formula X



wherein

n is an integer from 1 to 4, preferably an integer from 1 to 3, especially 2, and

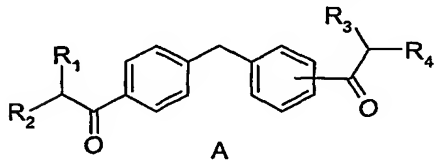
R_6 is an n-valent radical of linear or branched C_2-C_{16}alkyl the carbon chain of which may be interrupted by cyclohexanediyl, phenylene, -CH(OH)-, -C(CH_2-CH_2-OH)$_2$-, -C(CH_3)(CH_2-CH_2-OH)-, -C(C_2H_5)(CH_2-CH_2-OH)-, -N(CH_3)-, -N(CH_2-CH_2-OH)-, -CO-O-, -O-CO-, -O-CO-NH, NH-CO-O-, -Si(CH_3)$_2$-, -Si(CH_3)(R_{17})-O-Si(CH_3)(R_{18})-, -O-Si(CH_3)$_2$-O-, -O-Si(CH_3)(O-CH_3)-O-, 5-(2-hydroxyethyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl and / or by from one to six oxygen atoms, or

R_6 is an n-valent radical of linear or branched –C_2-C_{50}alkylene the carbon chain of which is interrupted by one to 15 oxygen, and may be subsituted by OH or NH_2;

R_8 is hydrogen, C_1-C_4alkyl,; C_2-C_4alkyl substituted by one or more of the groups OH, C_1-C_4alkoxy, -CN, -COO(C_1-C_4alkyl); C_3-C_5alkenyl, cyclohexyl or C_7-C_9phenylalkyl;

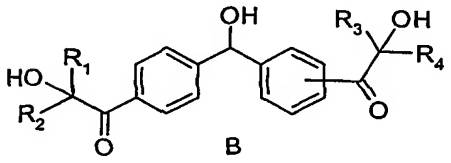
9. A process for the preparation of compound I or II, comprising the following steps:

a) reaction of diphenylmethane with an acid halide of formula R_1R_2CH-COHal and, optionally, further reaction with an acid halide of formula R_3R_4CH-COHal in the presence of a Friedel-Crafts catalyst, whereupon an isomeric mixture of formula A is obtained,



A

b) halogenation of the isomeric mixture of formula A, followed by bromination and hydrolysis, whereupon an isomeric mixture of formula B is obtained,



B

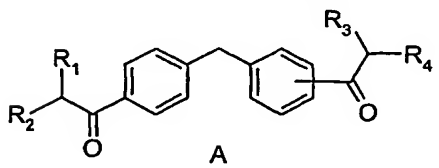
c) optionally, selective substitution of the benzylic hydroxy group in the resulting isomeric mixture of formula B by reaction
with an alcohol in the presence of an acid as catalyst for the preparation of an ether,
with a carboxylic acid for the preparation of an ester,
with an isocyanate for the preparation of a urethane,
with a diol, dicarboxylic acid or diisocyanate for the preparation of a bridged compound,
with a diisocyanate together with a diol or a diamine,
with a siloxane for the preparation of a silicone derivative,

d) optionally, reaction of the alpha-hydroxy group in the resulting isomeric mixture of formula B,

e) optionally, separation of the isomers.

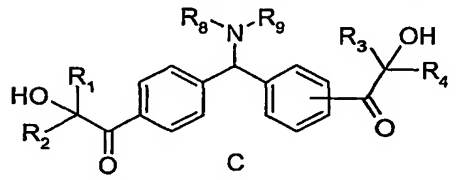
10. A process for the preparation of compound I or II, comprising the following steps:

a) reaction of diphenylmethane with an acid halide of formula R_1R_2CH-COHal and, optionally, further reaction with an acid halide of formula R_3R_4CH-COHal in the presence of a Friedel-Crafts catalyst, whereupon an isomeric mixture of formula A is obtained,



A

b) halogenation of the isomeric mixture of formula A, followed by bromination, aminolysis of the benzylic bromide, and hydrolysis of the tertiary halides, whereupon an isomeric mixture of formula C is obtained,



C

c) optionally, when R_8 or R_9 in the isomeric mixture of formula C possess a primary hydroxy group, selective substitution of the primary hydroxy group by reaction
with a carboxylic acid for the preparation of an ester,
with an isocyanate for the preparation of a urethane,
with a dicarboxylic acid or diisocyanate for the preparation of a bridged compound,
with a siloxane for the preparation of a silicone derivative

d) optionally, separation of the isomers.

11. A composition consisting of
(A) at least one ethylenically unsaturated compound,
(B) a photoinitiator of formula I, II, III, IV, V, VI, VII, VIII, IX or X according to claims 1-8
(C) optionally, further additives,
(D) optionally, further photoinitiators and coinitiators.

12. A composition according to claim 11, wherein the compound (A) is a resin containing free OH groups, free isocyanate groups or free carboxy groups and the photoinitiator (B) is bonded to the resin.

13. A process for the production of a scratch-resistant durable surface, wherein a composition according to either claim 11 or claim 12 is applied to a support; and curing of the formulation is carried out either solely by means of irradiation with electromagnetic radiation having a wavelength of from 200 nm into the IR range, or by irradiation with electromagnetic radiation and prior, simultaneous and/or subsequent application of heat.

14. Use of a composition according to claim 11 in the production of pigmented and non-pigmented surface coatings, overprint coatings, powder coatings, printing inks, inkjet inks, gel coats, composite materials or glass fibre coatings.

15. Use of a composition according to claim 12 as a surface coating for food packaging materials.